The Chemistry of Pyridine. VI. Steric and Electronic Effects Influencing the Deoxydative Substitution of Pyridine N-Oxides by Mercaptans in Acetic Anhydride

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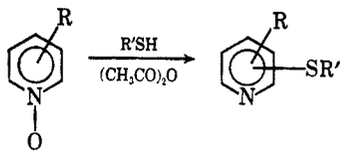
Received August 2, 1968

The deoxydative substitution of N-oxides derived from pyridine, 2-, 3-, and 4-picoline, 4-*t*-butylpyridine, 4-phenylpyridine, and 2,6-, 3,4-, and 3,5-lutidine by *t*-butyl mercaptan in acetic anhydride is reported. It was found that ring substitution introduced a *t*-butyl sulfide group at any one of the available α positions (2,6-lutidine 1-oxide being the exception) and only at those β positions which had originally a free α position adjacent to it. Mechanisms to explain both α and β substitution *via* 1-acetoxy-2-*t*-butylmercapto-1,2-dihydropyridines are postulated. Evidence is presented that β substitution involves migration of the sulfide function from such 1,2-dihydropyridines *via* episulfonium intermediates.

The discovery that pyridine N-oxides undergo deoxydative substitution by mercaptans in the presence of acylating agents to form pyridyl sulfides[2,3] warranted closer examination of certain phases of this reaction. Prior to this investigation, only two examples of this reaction in acetic anhydride had been described, that of pyridine 1-oxide with *n*-butyl mercaptan and of 4-picoline 1-oxide with *n*-propyl mercaptan. In both instances, α- and β-ring substitution took place.[2,3] This raised the question whether this substitution pattern of pyridine 1-oxides with mercaptans in acetic anhydride is a general one. To answer this immediate question, pyridine 1-oxide was subjected to methyl, *n*-propyl, and *t*-butyl mercaptans in acetic anhydride at 95° for 3 hr. The mixture of substituted pyridines obtained from each of these reactions was separated by preparative gas chromatography (gc), which permitted the isolation of additional components not observed in prior studies when only column chromatography was utilized.[2,3] In terms of substitution by mercaptans, these reactions yielded only 2- and 3-pyridyl sulfides (Table I) and their ratios were determined by integration of the corresponding gc peaks. Attempts to detect 4-pyridyl sulfides in the above and subsequent reactions, either as minor constituents or as contaminants in the more abundant fractions, proved futile. Other components[4] isolated from these reactions proved to be pyridyl acetates arising from either ring or active methylene substitutions.[6]

TABLE I



R	R'	Yield,[a] %	Isomer distribution of pyridyl sulfides 2-	3-	5-	6-
H	CH_3	38	52	48		
H	*n*-C_3H_7	46	76	24		
H	*n*-C_4H_9[f]	67	61	39		
H	*t*-C_4H_9	62	70	30		
2-CH_3	*t*-C_4H_9	32[b]			16	84
3-CH_3	*t*-C_4H_9	66	45		36	19
4-CH_3	*n*-C_3H_7[g]	31	50	50		
4-CH_3	*t*-C_4H_9	41[c]	71	29		
4-*t*-C_4H_9	*t*-C_4H_9	48	83	17		
4-C_6H_5	*t*-C_4H_9	18	44	56		
2,6-di-CH_3	*t*-C_4H_9	0[d]				
3,4-di-CH_3	*t*-C_4H_9	35[e]	48		29	23
3,4-di-CH_3	*t*-C_4H_9	66	100			

[a] Yields of ring substituted sulfides are based on starting N-oxide; the yield of active methylene-substituted sulfides are reported in footnotes *b–e*. [b] 10%. [c] 3%. [d] 1%. [e] 1%. [f] Reference 2. [g] Reference 3.

To establish the scope of this reaction more fully, a study involving a number of substituted pyridine N-oxides was initiated. Hence, the N-oxides of 2-, 3-, and 4-picoline, 4-*t*-butylpyridine, 4-phenylpyridine, and 2,6-, 3,4-, and 3,5-lutidine were treated with *t*-butyl mercaptan in acetic anhydride. This particular mercaptan was chosen for a number of reasons. It seemed plausible that its use might introduce steric effects and provide additional evidence for the mechanisms of these substitutions. For example, it remained to be determined if a bulky γ substituent on the pyridine ring, such as in 4-*t*-butylpyridine 1-oxide, would inhibit or prevent the entry of a *t*-butylmercapto group at the adjacent β ring carbon.

A further advantage was envisioned by the use of

(1) National Science Foundation Trainee, Sept 1965–Aug 1967. Taken from the Ph.D. Dissertation of F. M. H., University of Illinois at the Medical Center, Chicago, Ill., June 1968.

(2) L. Bauer and T. E. Dickerhofe, *J. Org. Chem.*, **29**, 2183 (1964).

(3) L. Bauer and A. L. Hirsch, *ibid.*, **31**, 1210 (1966).

(4) The reaction of pyridine N-oxides with acid anhydrides is receiving considerable attention. In a number of these reactions, the acid anhydride is transformed into other products with concomitant reduction of the N-oxide. In the present study, no attempt was made to look for similar aliphatic by-products or parent pyridines (see ref 5 for a leading paper).

(5) T. Cohen, I. H. Song, J. H. Fager, and G. L. Deets, *J. Amer. Chem. Soc.*, **89**, 4968 (1967).

(6) The conversion of pyridine N-oxides into either ring- or active methylene-substituted pyridyl esters is well documented (ref 5, 7–17). In the present work some of the esters isolated were identical with those reported from similar reactions in the absence of a mercaptan. However, some strikingly different but reproducible results were obtained from the reaction of pyridine N-oxide and acetic anhydride by using different mercaptans. For example, the reaction of pyridine N-oxide with acetic anhydride at the reflux (135–140°) furnished, as expected, 2-pyridyl acetate (ref 7) but at 95° for 3 hr no esters were isolated, most of the N-oxide being recovered. However, the inclusion of mercaptans in such a reaction mixture gave, under identical conditions, no 2-pyridyl acetate but some of the 3 or 4 isomer. It was found that in the presence of either *n*-propyl or *n*-butyl mercaptans some 3-pyridyl acetate was formed while with *t*-butyl mercaptan only 4-pyridyl acetate was isolated (see Experimental Section). The role of the thiol in changing this substitution pattern remains an enigma.

(7) E. Ochiai, "Aromatic N-Oxides," Elsevier Publishing Co., New York, N. Y., 1967.

(8) S. Oae, S. Tamagaki, T. Negoro, K. Ogino, and S. Kozuka, *Tetrahedron Lett.*, 917 (1968).

(9) R. Bodalski and A. R. Katritzky, *ibid.*, 257 (1968); *J. Chem. Soc., B*, 831 (1968).

(10) T. Cohen and G. L. Deets, *J. Amer. Chem. Soc.*, **89**, 3939 (1967).

(11) T. Koenig, *ibid.*, **88**, 4045 (1966).

(12) T. Cohen and J. H. Fager, *ibid.*, **87**, 5701 (1965).

(13) V. J. Traynelis and A. I. Gallagher, *ibid.*, **87**, 5710 (1965).

(14) C. Rüchardt and O. Krätz, *Tetrahedron Lett.*, 5915 (1966).

(15) P. W. Ford and J. M. Swan, *Aust. J. Chem.*, **18**, 867 (1965).

(16) C. W. Muth and R. S. Darlak, *J. Org. Chem.*, **30**, 1909 (1965).

(17) V. J. Traynelis, A. I. Gallagher, and R. F. Martello, *ibid.*, **26**, 4365 (1961).

t-butyl mercaptan. In the event that mixtures of *t*-butyl sulfides were obtained, unresolved by gc, it was hoped that proton magnetic resonance (pmr) spectroscopy might aid in the analysis of the components since *t*-butyl protons from each sulfide would be expected to appear as a single resonance line with somewhat different chemical shift. The sulfides isolated from the various N-oxides are listed in Table I, and their formation is discussed in terms of the over-all picture.

α Substitution.—During the course of substitution of the above-mentioned N-oxides by *t*-butyl mercaptan, one *t*-butyl thioether group was introduced at an available α position. If two different α positions presented themselves, two isomeric sulfides were obtained as was the case of unsymmetrical 3-picoline and 3,4-lutidine 1-oxides. Apparently a methyl group at the β ring carbon offered little or no steric encumbrance to attack by such a bulky nucleophile at the adjacent α position. At first glance, the data in Table I reveal that, in these two N-oxides, substitution at the more hindered site, C-2, with the methyl at C-3, is preferred (*ca.* 45%) to that at the other more exposed α carbon, C-6 (*ca.* 20%).[18] However, this ratio would have to be modified in view of the mechanism of β substitution (see below) and even then, in these two examples, attack at 2 and 6 would have been about equally popular.

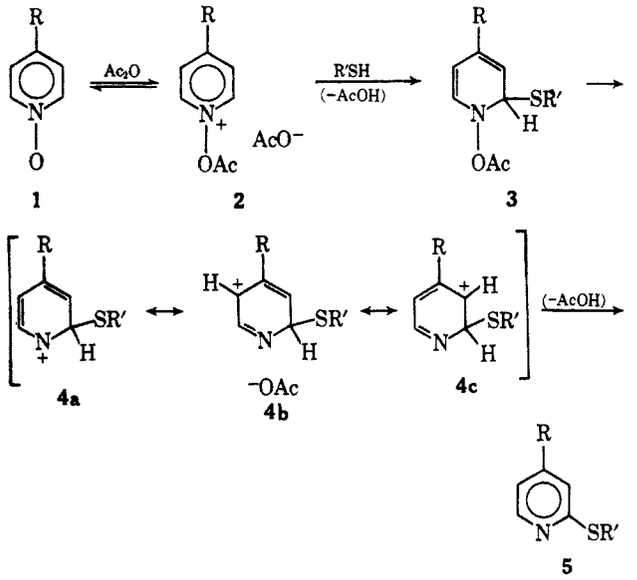
β Substitution.—Since a ring methyl group offers no particular hindrance to the entry of a *t*-butyl sulfide moiety next to it, one would predict that β substitution should be feasible at all such available positions. However, the reaction of 2-picoline 1-oxide with *t*-butyl mercaptan in acetic anhydride afforded only one β-substituted sulfide, *viz.*, 5-*t*-butylmercapto-2-picoline, and attempts to detect 3-*t*-butylmercapto-2-picoline proved futile. Similar substitution patterns were noticed in a number of related reactions. 2-Picoline 1-oxide and *n*-propyl mercaptan in the presence of benzenesulfonyl chloride yielded only 4-, 5-, and 6-propylmercapto-2-picolines (ratio of 6:42:52) and no 3-propylmercapto-2-picoline[3] and this pattern was repeated when *n*-butyl mercaptan was the thiol utilized.[19] The reaction of 2-methylmercaptopyridine 1-oxide with *n*-butyl mercaptan in boiling acetic anhydride only gave 4-, 5-, and 6-*n*-butylmercapto-2-methylmercaptopyridines (ratio of 3:33:64).[19]

It is appropriate to conclude that β substitution in this reaction requires initially a free adjacent α position. This point was strongly underscored when it was observed that no ring substitution took place at all with 2,6-lutidine 1-oxide under the conditions found favorable for picoline and other lutidine 1-oxides. This experiment would discount the possibility that β substitution arises from independent attack of the thiol on such a ring position. The last experiment lends strong support to the idea that β-pyridyl sulfides are the outcome of a rearrangement of an intermediate formed after the mercaptan attacks an adjacent α position.

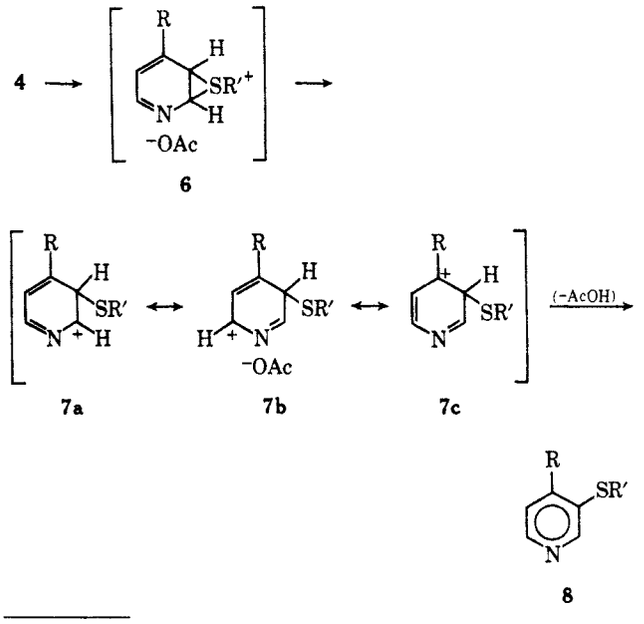
The N-oxides used in this investigation furnished sulfides owing to α (2 or 6) and selected β (3 or 5) ring substitution. No γ (4) substitution was observed and it appears unfavorable when acetic anhydride is the acylating agent. Whether the electrophilicity of the γ site cannot compete with that at the α carbons or whether the rate of aromatization of an intermediate formed at the γ ring carbon is relatively slow could be factors to account for virtually no γ substitution. Even with both α positions blocked as in 2,6-lutidine 1-oxide, no 4-*t*-butylmercapto-2,6-lutidine could be detected.[20]

Mechanism of Substitution.—Prior work on pyridine and picoline N-oxides involved a variety of quaternizing agents,[2,3,21] and mechanisms of substitution by mercaptans were advanced in general terms. In view of the observations in this and the ensuing paper,[22] more detailed mechanisms to explain α and β substitution in acetic anhydride are presented. These are illustrated in Schemes I and II, using a 4-substituted pyridine

SCHEME I



SCHEME II



(18) Preferred nucleophilic attack at a considerably more hindered α site is quite common in pyridine substitutions. For reviews, see R. A. Abramovitch and J. G. Saha, *Advan. Heterocycl. Chem.*, **6**, 274 (1966); R. A. Abramovitch and G. A. Poulton, *J. Chem. Soc., B*, 267 (1967).

(19) L. Bauer and T. L. Dickerhofe, unpublished work.

(20) Since no β or γ ring sulfide substitution was observed when 2,6-lutidine 1-oxide was treated with *n*-propyl mercaptan and benzenesulfonyl chloride,[3] similar mechanistic considerations may be involved.

(21) L. Bauer and L. A. Gardella, *J. Org. Chem.*, **28**, 1320 (1963).

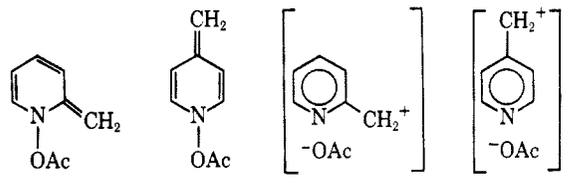
(22) F. M. Hershenson and L. Bauer, *ibid.*, **34**, 660 (1969).

1-oxide (**1**) as starting material. Since this substitution requires an acylating agent,[23] the first step is assumed to be the quaternization of **1**, to furnish the pyridinium salt (**2**) *in situ*[24] (CH_3CO is abbreviated to Ac throughout). Attack by thiol at the highly electrophilic α position of **2** leads to a 1,2-dihydropyridine (**3**). If aromatization of **3** would proceed by the abstraction of H-2 first or by the simultaneous loss of acetic acid, one could rationalize α but not β substitution from **3**. It is therefore postulated that the acetate ion separates *first* from **3** to create an *ion pair in a solvent cage*.[5,8-11] The resonance stabilized ion **4**, so formed, could then lose H-2 to complete the process of aromatization. The loss of acetic acid from **3** in this manner should be thermodynamically most favored since an aromatic 2-alkylmercaptopyridine (**5**) is produced. If **5** is formed from **4** in this manner, it could be that the slow step is the departure of H-2, presumably as a solvated ion which has to penetrate the solvent cage. This point is important if one is to consider a competing process from **3** which could account for β substitution. It is postulated that, with the separation of the acetate ion in **3**, the developing positive charge on the ring of **4** is neutralized by the participation of the nucleophilic sulfide group to create the episulfonium ion **6**. Although **6** could revert to **4**, its rearrangement to **7** would lead to β substitution. Two effects are in favor of the latter process. The inductive effect operating in **6** should weaken the C_α–S over the C_β–S bond, thereby facilitating the rearrangement to **7**. Perhaps the best driving force for the latter process is the formation of the carbonium ion **7** in which the charge is distributed over sp^2 C atoms, in contrast to **4** where some of the charge is localized (unfavorably so) onto the electrophilic nitrogen. Loss of H-3 in **7** would then furnish the aromatic 3-alkylmercaptopyridine **8.**

The best evidence for **6** was provided when a number of these reactions yielded tetrahydropyridines whose significant structural features were a sulfide group at one of the β ring carbons with an acetoxy group on the adjacent α carbon.[22] Some other points can be explained satisfactorily by this mechanism for β substitution. One of these concerns steric implications governing substitution at the β position when 4-substituted pyridine 1-oxides are employed. From the data in Table I, it is evident that the 4-methyl group in either 4-picoline or 3,4-lutidine 1-oxides offered little or no steric hindrance toward β substitution. These two N-oxides behaved as pyridine 1-oxide and, for each, entry of a *t*-butyl sulfide group at C-3 took place to the extent of about 30% of all ring substitution. Apparently, the 4-*t*-butyl group exerted some steric hindrance judging by the reduced amount of β substitution (17% of the total sulfides). This is still quite remarkable since it does mean that a bulky group could be introduced next to a *t*-butyl group under such mild conditions.[25]

The substitution of 4-phenylpyridine 1-oxide was not accomplished at 95° but proceeded at 140°, albeit in relatively poor yield. The fact that better than half of the ring sulfides (Table I) were the result of β substitution can be explained well by the mechanism in Scheme II. The presence of the phenyl group may very well influence the mode of ring opening of **6** (R = C_6H_5; R′ = *t*-C_4H_9) as suggested to **7**, since it would involve also the benzyl carbonium ion, **7c.** This factor might be responsible for the large amount of β substitution. This point will be tested experimentally by using a number of substituted (in the benzene ring) 4-arylpyridine 1-oxides.

Active Methylene Substitutions.—The present investigation also encountered some active methylene substitution in α- or γ-methyl groups of the picoline and lutidine N-oxides. It has been demonstrated distinctly that, during the reaction of 2- and 4-picoline 1-oxides in acetic anhydride, *both* active methylene and β ring substitution by acetate ion takes place *via* anhydro bases **9** and **10,** or more exactly *via ion pairs in a solvent cage*, **11** and **12.**[5,8-13] In the present work, active methylene substitution by both mercaptan and acetate



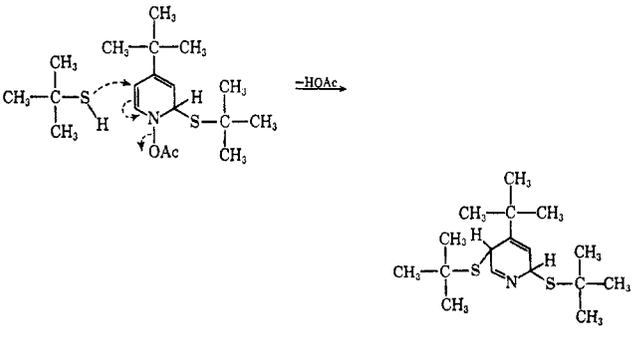
9 **10** **11** **12**

was encountered. It would appear reasonable to suppose that active methylene substitution of 2- and 4-picoline 1-oxides by thiol or carboxylate ion proceeds *via* **9** (or **11**) and **10** (or **12**), respectively. However, it is quite unlikely that β ring substitution by mercaptans of active methylene-containing pyridine N-oxides takes place *via* their cognate anhydro bases (or corresponding *ion pairs*). Whereas it is an inviting analogy to consider β substitution of 2- and 4-picoline 1-oxides by thiol *via* **9** (or **11**) or **10** (or **12**), it is more likely to take place by the mechanism considered in Scheme II. Several facts support such a hypothesis. When 2,6-lutidine 1-oxide is exposed to *t*-butyl mercaptan in acetic anhydride the thiol does not attack the β ring position at all, in contrast to acetate ion which gives 3-(2,6-dimethyl)pyridyl acetate (about 30% of the esters isolated).[26] The premise that β substitution

(23) Pyridine N-oxides were simply reduced by thiols but not substituted: D. I. Relyea, P. O. Tawney, and A. R. Williams, *J. Org. Chem.*, **27,** 477 (1962).

(24) There is ample evidence for the formation of 1-acetoxypyridinium salts. A number of these were isolated as the perchlorates[16] or picrates.[17]

(25) This experiment tends to rule out an alternate mechanism for β substitution which would require attack by a second mole of thiol on the 1,2-dihydropyridine, **2** (R = R′ = *t*-C_4H_9), at C-3 or C-5 with the departure of the acetate group.



Such an attack at the less hindered C-5 position, for example, would yield a 2,5-dihydropyridine (as shown) which would still have to lose *t*-butyl mercaptan to form either 2- or 3-*t*-butylmercapto-4-*t*-butylpyridine. This type of mechanism has been suggested to explain some β substitutions (not necessarily those by mercaptans) of pyridine 1-oxides (ref 2, footnote 11).

(26) Such a β substitution of 2,6-lutidine 1-oxide in acetic anhydride was reported by T. Kato, T. Kitagawa, T. Shibata, and K. Nakai [*J. Pharm. Soc. Jap.*, **82,** 1647 (1962)].

by mercaptans takes place independent of active methylene groups is reinforced when it was shown that 3-picoline and 4-*t*-butyl- and 4-phenylpyridine 1-oxides gave 3-substituted pyridyl sulfides (Table I). In the last three examples, anhydro base formation is not plausible. By the same token, from the reactions of these N-oxides, no corresponding 3-pyridyl acetates were isolated. Thus, it would appear that β substitution of N-oxides by an acetate group is only conceivable if an active methylene group is originally present on the ring, but this is not a requirement for β substitution by thiols.

Structure Determination.—The products isolated from the above reactions were characterized by their spectra. Most of the sulfides and esters possessed easily recognizable molecular ions and had their formula confirmed (if new) by elemental analyses. To settle the substitution pattern in the pyridines, pmr spectroscopy was resorted to. The chemical shifts and coupling constants in pyridines are established[3,27,28] well enough to permit assignment of the structures based on the data listed in the Experimental Section. In several instances, authentic samples were synthesized since the sample isolated from the substitution reactions was too small. 4-*t*-Butylmercaptopyridine was prepared from 4-chloropyridine to provide authentic spectra and gc characteristics and ensure that its presence could be detected if it was formed from pyridine N-oxide and *t*-butyl mercaptan in acetic anhydride.

Experimental Section[29]

Starting Materials.—Generous gifts of the following chemicals are most gratefully acknowledged: *t*-butyl mercaptan[30] from Pennsalt Chemical Co. and Phillips Petroleum Co.; methyl mercaptan from Amoco Chemical Corp.; 4-*t*-butylpyridine, pyridine-, 2-, 3-, and 4-picoline 1-oxides and 2,6-lutidine 1-oxide from Reilly Tar and Chemical Co. 4-Phenylpyridine, 4-chloropyridine hydrochloride, 2-picolyl chloride hydrochloride, 6-methyl-2-picolyl chloride hydrochloride, and 3,4- and 3,5-lutidines were purchased from Aldrich Chemical Co. Alumina used throughout this work was purchased from Alcoa (Grade F-20); benzene for chromatography was thiophene-free; petroleum ether was that fraction of bp 30–60°.

The N-oxides utilized in this work were prepared by the standard oxidation,[31] but the mode of isolation was changed somewhat. Instead of destroying the excess peroxide by repeated evaporations, *in vacuo*, the base was extracted after making the reaction mixture alkaline. A typical example is presented.

3,5-Lutidine 1-Oxide.—A solution of 3,5-lutidine (53.5 g, 0.5 mol) in acetic acid (300 ml) was stirred at 90°, while 30% H_2O_2 (50 ml) was added dropwise over 0.5 hr. The solution was stirred at 90° for 3 hr and an additional portion of 30% H_2O_2 (35 ml) was then added dropwise. The solution was stirred at 90° for 19 hr, then cooled, and made basic with 50% aqueous NaOH (250 ml). The basic solution was extracted repeatedly with $CHCl_3$. Evaporation of $CHCl_3$, *in vacuo*, yielded a solid which was crystallized from ethyl acetate to furnish light tan needles (18.4 g, 30%), mp 101–102°. This product had previously been described as a hygroscopic oil[32] or a hygroscopic solid,[33] mp 85°.

Anal. Calcd for C_7H_9NO: N, 11.38. Found: N, 11.40.

By this method, there were prepared 4-*t*-butylpyridine 1-oxide (68%, mp 101–102°, lit.[34] mp 103.9–104.3°), 4-phenylpyridine 1-oxide (85%, mp 150–152°, lit.[35] mp 151–152°), and 3,4-lutidine 1-oxide (42%, mp 127–128°, lit.[36] mp 128–130°).

Reference Compounds. 4-*t*-Butylmercaptopyridine.—A 51.5% suspension of sodium hydride (9.4 g, 0.2 mol) in mineral oil (Metal Hydrides, Inc.) was suspended in N,N-dimethylformamide (100 ml). The mixture was stirred at 5° while *t*-butyl mercaptan (21.5 ml, 0.2 mol) was added dropwise, followed by 4-chloropyridine hydrochloride (15.0 g, 0.1 mol) in small portions. The reaction mixture was heated to 95° for 3.5 hr and then poured onto a slurry of concentrated HCl and ice (pH <2). The solution was concentrated *in vacuo*, and the residue was dissolved in dilute HCl, 1:3 (50 ml). The acidic solution was extracted with benzene–ether, 1:1 (three 50-ml portions), and then made alkaline by 20% NaOH (90 ml) (pH 11). Extraction of this basic solution with CH_2Cl_2 (five 50-ml portions) yielded the product (7.95 g, 48%) of bp 64–65° (0.2 mm); pmr ($CDCl_3$) aromatic H's as AA'XX' pattern (encountered in a number of 4-substituted pyridines below), δ 8.50 (m, H-2, H-6), 7.33 (m, H-3, H-5), and 1.31 (*t*-C_4H_9).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.87; H, 8.12; N, 8.49.

4-Picolyl *t*-Butyl Sulfide.—Reaction of 4-picolyl chloride hydrochloride (16.4 g, 0.2 mol) with *t*-butyl mercaptan as described immediately above yielded the product (13.2 g, 73%) of bp 70–71° (0.25 mm); pmr ($CDCl_3$) δ 8.40 (m, H-2, H-6), 7.23 (m, H-3, H-5), 3.48 (CH_2S), 1.27 (*t*-C_4H_9).

Anal. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.09; H, 8.35; N, 7.61.

2-(*t*-Butylmercapto)methyl-6-picoline.—A similar reaction of 6-methyl-2-picolyl chloride hydrochloride (17.8 g, 0.2 mol) with *t*-butyl mercaptan as described above furnished the requisite **sulfide** (77%): bp 71–72° (0.4 mm); pmr ($CDCl_3$) δ 7.63–6.75 (m, aromatic H), 3.83 (CH_2S), 2.43 (6-CH_3), 1.27 (*t*-C_4H_9).

Anal. Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.77; H, 8.99; N, 7.45.

Reaction of N-Oxides with Mercaptans in the Presence of Acetic Anhydride. A. Pyridine 1-Oxide and *t*-Butyl Mercaptan.—Acetic anhydride (300 ml) was added to a mixture of pyridine 1-oxide (28.5 g, 0.3 mol) and *t*-butyl mercaptan (96 ml, 0.9 mol) and the resultant solution was heated on a steam bath (95°) for 3 hr. The solution was cooled somewhat and a low boiling fraction was distilled at 95° (steam bath) *in vacuo* (20–30 mm). This liquid was not examined further.[30] Further fractionation yielded a colorless oil (33.9 g), bp 50–55° (0.2

(27) C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocycl. Chem.*, **2**, 420 (1965).

(28) W. Brügel, *Z. Electrochem.*, **66**, 159 (1962).

(29) Melting and boiling points are uncorrected. Microanalyses were performed by Dr. Kurt Eder, Geneva, Switzerland, and by Micro-Tech Laboratories, Inc., Skokie, Ill. Some of the nitrogen analyses were determined by the late Mr. Leo Horner in this department using a Coleman Nitrogen Analyzer, Model 29. Ir spectra were obtained in CCl_4 solution with a Perkin–Elmer Model 337 recording spectrophotometer. Pmr spectra were taken at 60 MHz with a Varian A-60 spectrometer. Signals are reported in parts per million (δ) downfield from internal tetramethylsilane (TMS) or organic solvents, or from sodium 3-(trimethylsilyl)-1-propanesulfonate (TPS), in D_2O solution. Each A-60 spectrum was calibrated by a sample of TMS (δ 0) in $CHCl_3$ (δ 7.28). Proton assignment was based on correct integral information, on chemical shifts anticipated for the particular protons, and, whenever possible, on spin–spin coupling constants (J) derived from first-order analysis. Whenever δ and J are reported, multiplicities are omitted, these being assumed to be those expected from first-order analysis; when the multiplicities are described, the standard abbreviations (see "Notice to Authors") are utilized.

(30) This mercaptan has to be handled with extreme care to prevent panic since its presence in the atmosphere in extremely low concentrations is mistaken for a "gas leak;" it is, of course, a contaminant deliberately added to natural gas for the very purpose of detecting such leaks. It was almost impossible to prevent these near panics since hood exhausts (or vent stacks over sewer traps at the bottom of the drains in the building) distributed the gas onto the roof of the building. Some of this polluted air apparently was sucked into the ventilation system of the building and, even worse, into that of the Research Hospital across the street. To prevent this alarming confusion, as much as possible, all reactions were carried out under an efficient hood, with lead-off tubes into a Dry Ice trap both during the conduct of these reactions under reflux and during the evaporation (*in vacuo*) of the lowest boiling fraction at the end of the reaction. Distillates containing this mercaptan and also the contents of the cold-finger traps were always decomposed by the slow addition to a *large* excess of an aqueous *saturated* $KMnO_4$ solution to effect oxidation of the mercaptan. The oxidized mixture posed no problem and could be disposed down the drain.

(31) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(32) J. M. Essery and K. Schofield, *J. Chem. Soc.*, 4953 (1960).

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mm). The bath temperature during this distillation was never allowed to exceed 110°. By means of gc[37] of the higher boiling distillate the following components were collected (injection temperature 95°).

4-Pyridyl acetate (9%, rt 26.7 min): mp 142–143° (lit.[38] mp 135–140°, 140–150°); ir ($CHCl_3$) 1770 cm^{-1} (C=O); pmr (D_2O) δ 8.06 (m, H-2, H-6), 6.77 (m, H-3, H-5), 2.13 (CH_3).

2-*t*-Butylmercaptopyridine (64%, rt 37.0 min): pmr ($CDCl_3$) δ 7.28 (H-3), 7.52 (H-4), 7.03 (H-5), 8.53 (H-6), ($J_{3,5}$ = 2.0, $J_{4,5}$ = 6.6, $J_{4,6}$ = 1.8, $J_{5,6}$ = 4.8, $J_{3,6}$ = 1.0 Hz), 1.53 (t-C_4H_9). *Anal.* Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.85; H, 8.00; N, 8.26.

3-*t*-Butylmercaptopyridine (27%, rt 39.2 min): pmr ($CDCl_3$) δ 8.72 (H-2), 8.58 (H-6), 7.92 (H-4), 7.25 (H-5), ($J_{2,4}$ = 2.2, $J_{4,5}$ = 7.9, $J_{4,6}$ = 1.6, $J_{5,6}$ = 4.8, $J_{2,5}$ = 0.8 Hz), 1.28 (t-C_4H_9). *Anal.* Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.68; H, 7.91; N, 8.13.

Based on the N-oxide, the yield of sulfides was 62% and that of 4-pyridyl acetate was 7%.

B. Pyridine 1-Oxide and *n*-Propyl Mercaptan.—The reaction as described under A (on 0.1 mol of pyridine 1-oxide) gave, on work-up, an oil (8.2 g), bp 48–52° (0.25 mm). Gc separation[37] (injection temperature 95°) yielded three components.

3-Pyridyl acetate (14.4%, rt 30.0 min): ir (film) 1770 cm^{-1} (C=O); pmr ($CDCl_3$) δ 8.53–8.33 (m, H-2, H-6), 7.50–7.17 (m, H-4, H-5), 2.32 (CH_3).

2-*n*-Propylmercaptopyridine (65.0%, rt 43.9 min): ir identical with that of an authentic sample:[21] pmr ($CDCl_3$) δ 8.38 (H-6), 7.38 (H-4), 7.00 (H-3), 6.87 (H-5), 3.13 (CH_2S), 1.71 (CH_2), 1.00 (CH_3).

3-*n*-Propylmercaptopyridine (20.6%, rt 47.2 min): ir identical with that of an authentic sample:[21] pmr ($CDCl_3$) δ 8.55 (H-6), 8.40 (H-2), 7.63 (H-4), 7.16 (H-5), 2.91 (CH_2S), 1.68 (CH_2), 1.02 (CH_3).

Based on the N-oxide, the yield of sulfides was 46%, that of the ester was 9%.

C. Pyridine 1-Oxide and Methyl Mercaptan.—Methyl mercaptan was bubbled through a stirred solution of pyridine 1-oxide (9.5 g, 0.1 mol) in acetic anhydride (100 ml) at 5° for 0.25 hr, then at 25° for 0.5 hr. The solution was brought to boil for 1 hr while the mercaptan was continued to be bubbled through the reaction mixture. After 2-hr additional heating at the reflux, the reaction was worked up as usual (see A) and the oil (4.82 g), bp 59–70° (2.5 mm), was collected. Gc separation[37] (injection temperature 105°) yielded the following components.

2-Methylmercaptopyridine (51.8%, rt 42.6 min): pmr ($CDCl_3$) δ 8.18 (H-6), 7.27 (H-4), 6.93 (H-3), 6.73 (H-5) ($J_{3,4}$ = 7.9, $J_{3,5}$ = 1.8, $J_{4,5}$ = 6.8, $J_{4,6}$ = 1.8, $J_{5,6}$ = 5.2, $J_{3,6}$ = 1.0 Hz), 2.47 (CH_3S). *Anal.* Calcd for C_6H_7NS: C, 57.60; H, 5.60; N, 11.20. Found: C, 57.61; H, 5.74; N, 11.46.

3-Methylmercaptopyridine (48.2%, rt 46.8 min): pmr ($CDCl_3$) δ 8.23 (H-6), 8.10 (H-2), 7.32 (H-4), 6.95 (H-5) ($J_{2,4}$ = 2.2, $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.6, $J_{5,6}$ = 4.6, $J_{2,5}$ = 0.8 Hz), 2.38 (CH_3S). *Anal.* Calcd for C_6H_7NS: C, 57.60; H, 5.60; N, 11.20. Found: C, 57.34; H, 5.65; N, 11.23.

D. 4-Picoline 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 4-picoline 1-oxide (0.3 mol) as described under A yielded a fraction (34.6 g) of bp 57–62° (0.15 mm) which was separated by gc[37] (injection temperature 140°) and found to contain the following components.

3-Acetoxy-4-picoline (10.9%, rt 22.4 min): ir ($CHCl_3$) 1750 cm^{-1} (C=O); pmr ($CDCl_3$) δ 8.53–8.33 (m, H-2, H-6), 7.25–7.08 (m, H-5), 2.30 (4-CH_3), 2.17 (CH_3CO_2).

4-Picolyl acetate (20.4%, rt 24.3 min): ir ($CHCl_3$) 1755 cm^{-1} (C=O); pmr ($CDCl_3$) δ 8.56–8.37 (m, H-2, H-6), 7.20–7.03 (m, H-3, H-5), 5.08 (4-CH_2O), 2.12 (CH_3CO_2).

2-*t*-Butylmercapto-4-picoline (44.9%, rt 34.7 min): pmr ($CDCl_3$) δ 8.32 (H-6), 7.13 (H-3), 6.88 (H-5) ($J_{3,5}$ = 1.3, $J_{5,6}$ = 4.4 Hz), 2.23 (4-CH_3), 1.47 (t-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.18; H, 8.22; N, 7.92.

3-*t*-Butylmercapto-4-picoline (18.6%, rt 38.1 min): pmr ($CDCl_3$) δ 8.63 (H-2), 8.38 (H-6), 7.18 (H-5) ($J_{5,6}$ = 4.3 Hz), 2.48 (4-CH_3), 1.27 (t-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 65.96; H, 8.44; N, 7.57.

4-Picolyl *t*-butyl sulfide (5.2%, rt 42.1 min): ir spectrum identical with that of an authentic sample described above.

Based on the N-oxide, the yield of sulfides was 44%, that of the esters was 24%.

E. 4-*t*-Butylpyridine 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 4-*t*-butylpyridine 1-oxide (0.1 mol) as described under A yielded a fraction (10.6 g) of bp 92–96° (0.4 mm) which was separated by gc[37] (injection temperature 110°) and found to contain the following components.

2-*t*-Butylmercapto-4-*t*-butylpyridine (82.9%, rt 47.8 min): pmr ($CDCl_3$) δ 8.48 (H-6), 7.37 (H-3), 7.12 (H-5) ($J_{3,5}$ = 1.8, $J_{5,6}$ = 5.1, $J_{3,6}$ = 0.7 Hz), 1.50 (t-C_4H_9S), 1.25 (t-C_4H_9). *Anal.* Calcd for $C_{13}H_{21}NS$: C, 69.90; H, 9.48; N, 6.27. Found: C, 69.77; H, 9.36; N, 5.99.

3-*t*-Butylmercapto-4-*t*-butylpyridine (17.1%, rt 53.2 min): pmr ($CDCl_3$) δ 8.58 (H-2), 8.30 (H-6), 7.20 (H-5) ($J_{5,6}$ = 5.0 Hz), 1.47 (t-C_4H_9S), 1.35 (t-C_4H_9). *Anal.* Calcd for $C_{13}H_{21}NS$: C, 69.90; H, 9.48; N, 6.27. Found: C, 69.65; H, 9.74; N, 6.13.

F. 4-Phenylpyridine 1-Oxide with *t*-Butyl Mercaptan.—Acetic anhydride (100 ml) was added to a mixture of 4-phenylpyridine 1-oxide (15.5 g, 0.1 mol) and *t*-butyl mercaptan (32 ml, 0.3 mol) and the resultant solution was heated to reflux for 2 hr. The reaction mixture was then worked up as described under A yielding a light yellow oil, bp 103–108° (0.3 mm). On cooling, a white solid precipitated from this oil. This solid was collected (3.1 g), mp 69–70°, and its ir spectrum was identical with that of an authentic sample of 4-phenylpyridine. The yellow mother liquor (6.15 g) was separated by gc[37] (injection temperature 100°) and found to contain the following components.

4-Phenylpyridine (27.9%, rt 65.2 min): ir spectrum identical with that of an authentic sample.

3-*t*-Butylmercapto-4-phenylpyridine (40.6%, rt 110.0 min): pmr ($CDCl_3$) δ 8.58 (H-2), 8.32 (H-6), 7.08 (H-5) ($J_{5,6}$ = 4.6, $J_{2,5}$ = 0.6 Hz), 7.18 (m, C_6H_5), 0.98 (t-C_4H_9). *Anal.* Calcd for $C_{15}H_{17}NS$: C, 74.07; H, 6.99; N, 5.76. Found: C, 74.13; H, 7.01; N, 5.69.

2-*t*-Butylmercapto-4-phenylpyridine (31.5%, rt 126.5 min): pmr ($CDCl_3$) δ 8.33 (H-6), 7.50–7.00 (m, H-3, H-5, C_6H_5) ($J_{5,6}$ = 4.7, $J_{3,6}$ = 0.6 Hz), 1.48 (t-C_4H_9). *Anal.* Calcd for $C_{15}H_{17}NS$: C, 74.07; H, 6.99; N, 5.76. Found: C, 73.83; H, 7.16; N, 5.78.

G. 2-Picoline 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 2-picoline 1-oxide (0.3 mol) as described under A yielded a fraction (40.25 g) of bp 62–67° (0.1 mm) which was separated by gc[37] (injection temperature 70°) and found to contain the following components.

2-Picolyl acetate (34.2%, rt 46.7 min): pmr ($CDCl_3$) δ 8.60–8.43 (m, H-6), 7.75–6.97 (m, H-3, H-4, H-5), 5.17 (CH_2O), 2.08 (CH_3CO_2).

6-*t*-Butylmercapto-2-picoline (36.5%, rt 56.4 min): pmr ($CDCl_3$) δ 7.10 (H-4), 6.88, 6.68 (H-3, H-5) ($J_{3,4}$ = $J_{4,5}$ = 7.3, $J_{3,5}$ = 1.2 Hz), 2.28 (CH_3), 1.42 (t-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.50; H, 8.36; N, 7.78.

5-*t*-Butylmercapto-2-picoline (7.1%, rt 60.0 min): pmr ($CDCl_3$) δ 8.47 (H-6), 7.47 (H-4), 6.88 (H-3) ($J_{3,4}$ = 7.4, $J_{4,6}$ = 1.9, $J_{3,6}$ = 0.5 Hz), 2.48 (CH_3), 1.23 (t-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.00; H, 8.22; N, 8.01.

2-Picolyl *t*-butyl sulfide (13.5%, rt 63.9 min): pmr ($CDCl_3$) δ 8.22 (H-6), 7.36 (H-4), 7.15 (H-3), 6.85 (H-5) ($J_{3,4}$ = 7.8, $J_{3,5}$ = 1.8, $J_{4,5}$ = 6.8, $J_{4,6}$ = 1.8, $J_{5,6}$ = 4.9, $J_{3,6}$ = 1.0 Hz), 3.80 (CH_2), 1.28 (t-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.06; H, 8.27; N, 7.99.

On the basis of these results, the total yield of picolyl sulfides in this reaction was 42% and that of picolyl esters was 30%.

H. 3-Picoline 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 3-picoline 1-oxide (0.3 mol) as described under A yielded an oil (37.5 g) of bp 73–75° (0.15 mm) which was separated by gc[37] (injection temperature 70°) and found to contain the following components.

(37) Preparative gas chromatography (gc) was carried out by means of a Varian Aerograph Autoprep Model 700 chromatograph, using a 20 ft × ⅜ in. coiled aluminum column, packed with 20% silicon rubber gum (SE-30) on Chromosorb (40–60 mesh). Injection (0.1 to 0.25 ml) was performed at temperatures stated and helium was used as carrier gas at 200 ml/min. Each run was nonlinearly temperature programmed at the "45" power setting of the instrument. The composition of the mixture injected is expressed in mole per cent for each compound. Retention times (rt) are quoted for a particular run reported here.

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2-*t*-Butylmercapto-3-picoline (43.5%, rt 59.8 min): pmr ($CDCl_3$) δ 8.07 (H-6), 7.05 (H-4), 6.63 (H-5) ($J_{4,5}$ = 7.1, $J_{4,6}$ = 1.8, $J_{5,6}$ = 4.7 Hz), 2.18 (CH_3), 1.53 (*t*-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.57, H, 8.44; N, 7.57.

2-*t*-Butylmercapto-5-picoline (17.9%, rt 63.4 min): pmr ($CDCl_3$) δ 8.10 (H-6), 7.10 (H-3, H-4, br m), 2.22 (CH_3), 1.40 (*t*-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.78; H, 8.46; N, 7.69.

3-*t*-Butylmercapto-5-picoline (34.8%, rt 67.0 min): pmr ($CDCl_3$) δ 8.22, 8.13 (H-2, H-6), 7.42 (H-4) ($J_{2,4}$ = $J_{4,6}$ = 1.3 Hz), 2.27 (CH_3), 1.25 (*t*-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.20; H, 8.54; N, 7.69.

I. 3,5-Lutidine 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 3,5-lutidine 1-oxide (0.1 mol) as described under A provided an oil (12.8 g) of bp 56–58° (0.1 mm). Gc[37] examination of this oil revealed only one component which was **2-*t*-butylmercapto-3,5-lutidine**: pmr ($CDCl_3$) δ 8.08 (H-6), 7.07 (H-4) ($J_{4,6}$ = 2.0 Hz), 2.20, 2.17 (CH_3), 1.53 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.79; H, 8.66; N, 7.01.

J. 3,4-Lutidine 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 3,4-lutidine 1-oxide (0.1 mol) as described under A provided an oil (9.0 g) of bp 90–91° (0.1 mm) which was separated by gc[37] (injection temperature 150°) and found to contain the following components.

(3-Methyl-4-pyridine)methyl acetate (21.5%, rt 44.5 min): pmr ($CDCl_3$) δ 8.30 (H-2), 8.10 (H-6), 7.17 (H-5), 5.05 (4-CH_2O), 2.27 (3-CH_3), 2.13 (CH_3CO_2).

2-*t*-Butylmercapto-3,4-lutidine (36.2%, rt 56.8 min): pmr ($CDCl_3$) δ 7.90 (H-6), 6.55 (H-5) ($J_{5,6}$ = 4.5 Hz), 2.13 (CH_3), 1.50 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.69; H, 8.77; N, 7.29.

2-*t*-Butylmercapto-4,5-lutidine (17.3%, rt 60.4 min): pmr ($CDCl_3$) δ 8.00 (H-6), 6.95 (H-3), 2.13 (CH_3), 1.40 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.45; H, 8.73; N, 7.21.

3-*t*-Butylmercapto-4,5-lutidine (21.7%, rt 64.8 min): pmr ($CDCl_3$) δ 8.30, 8.05 (H-2, H-6), 2.40, 2.20 (CH_3), 1.23 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.59; H, 8.86; N, 6.94.

4-(*t*-Butylmercapto)methyl-3-picoline (3.3%, rt 67.2 min): pmr ($CDCl_3$) δ 8.12 (H-2, H-6), 6.98 (H-5), 3.88 (CH_2), 2.30 (CH_3), 1.33 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.68; H, 8.68; N, 7.20.

Based on the N-oxide, the total yield of sulfides was 36% and that of pyridyl esters was 11%.

K. 2,6-Lutidine 1-Oxide with *t*-Butyl Mercaptan.—The reaction was carried out with 2,6-lutidine 1-oxide (0.1 mol) as described under A and yielded an oil (8.2 g) of bp 75–78° (0.1 mm) which was separated by gc[37] (injection temperature 110°) and found to contain the following components.

3-(2,6-Dimethyl)pyridyl acetate (29.5%, rt 39.0 min): pmr ($CDCl_3$) δ 7.10 (H-3, H-4, center of AB quartet), 2.50, 2.40 (2-CH_3, 6-CH_3), 2.30 (CH_3CO_2).

(6-Methyl-2-pyridine)methyl acetate (65.6%, rt 43.6 min): pmr ($CDCl_3$) δ 6.92–7.67 (H-3, H-4, H-5), 5.15 (2-CH_2O), 2.50 (6-CH_3), 2.08 (CH_3CO_2).

2-(*t*-Butylmercapto)methyl-6-picoline (3.0%, rt 55.8 min): pmr ($CDCl_3$) δ 7.15, 6.88 (H-3, H-5), 7.43 (H-4) ($J_{3,4}$ = $J_{4,5}$ = 7.5, $J_{3,5}$ = 1.4 Hz), 3.83 (CH_2), 2.43 (CH_3), 1.27 (*t*-C_4H_9); ir spectrum identical with that of an authentic sample, whose preparation is described above.

Based on the starting N-oxide, the total yield of lutidyl sulfides was 1% and of lutidyl acetates was 47%.

Registry No.—4-*t*-Butylmercaptopyridine, 18794-26-8; 4-picolyl *t*-butyl sulfide, 18794-27-9; 2-(*t*-butylmercapto)methyl-6-picoline, 18794-28-0; 2-*t*-butylmercaptopyridine, 18794-29-1; 3-*t*-butylmercaptopyridine, 18794-30-4; 3-pyridyl acetate, 17747-43-2; 2-methylmercaptopyridine, 18434-38-5; 3-methylmercaptopyridine, 18794-33-7; 3-acetoxy-4-picoline, 1006-96-8; 4-picolyl acetate, 1007-48-3; 2-*t*-butylmercapto-4-picoline, 18794-36-0; 3-*t*-butylmercapto-4-picoline, 18794-37-1; 2-*t*-butylmercapto-4-*t*-butylpyridine, 18794-38-2; 3-*t*-butylmercapto-4-*t*-butylpyridine, 18794-39-3; 3-*t*-butylmercapto-4-phenylpyridine, 18794-40-6; 2-*t*-butylmercapto-4-phenylpyridine, 18794-41-7; 2-picolyl acetate, 1007-49-4; 6-*t*-butylmercapto-2-picoline, 18794-43-9; 5-*t*-butylmercapto-2-picoline, 18794-44-0; 2-picolyl *t*-butyl sulfide, 18794-45-1; 2-*t*-butylmercapto-3-picoline, 18833-87-9; 2-*t*-butylmercapto-5-picoline, 18794-46-2; 3-*t*-butylmercapto-5-picoline, 18794-47-3; 2-*t*-butylmercapto-3,5-lutidine, 18794-48-4; (3-methyl-4-pyridine)methyl acetate, 18794-49-5; 2-*t*-butylmercapto-3,4-lutidine, 18794-50-8; 2-*t*-butylmercapto-4,5-lutidine, 18794-51-9; 3-*t*-butylmercapto-4,5-lutidine, 18794-52-0; 4-(*t*-butylmercapto)methyl-3-picoline, 18794-53-1; 3-(2,6-dimethyl)pyridyl acetate, 18794-54-2; (6-methyl-2-pyridine)methyl acetate, 13287-64-4; 2-(*t*-butylmercapto)methyl-6-picoline, 18794-28-0; acetic anhydride, 108-24-7.

The Chemistry of Pyridine. VII. Tetrahydropyridines from the Reaction of Pyridine N-Oxides with Mercaptans in Acetic Anhydride

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Received August 2, 1968

A number of solids isolated from the reaction of pyridine N-oxides with mercaptans in acetic anhydride were shown to be 1-acetyl-1,2,3,6-tetrahydropyridines. One feature common to these compounds was that a sulfide group was attached to the β sp^3 ring carbon while both the α positions on the ring were substituted by either sulfide or acetoxy groups. The formation of these products is discussed in terms of the episulfonium intermediate proposed in the prior paper.[2]

Structure proofs are presented for a number of crystalline high molecular weight by-products isolated from the reaction of the N-oxides of pyridine, 4-picoline, 4-*t*-butylpyridine, 4-phenylpyridine, and 3,5-lutidine with *t*-butyl mercaptan in acetic anhydride.[2] A similar product was obtained from pyridine 1-oxide, methyl mercaptan, and acetic anhydride.[2] Spectral data confirm these compounds to be the tetrahydropyridines, **1a–d** and **11–13** (CH_3CO abbreviated to Ac throughout). In these piperideines, alkyl or aryl groups

(1) National Science Foundation Trainee. Abstracted from the Ph.D. Dissertation of F. M. H., University of Illinois at the Medical Center, Chicago, Ill., June 1968.

(2) F. M. Hershenson and L. Bauer, *J. Org. Chem.*, **34**, 655 (1969).